Abiotic Dechlorination in Clay to Support Natural Attenuation

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Background/Objectives. The naturally occurring abiotic dechlorination of chlorinated solvents in clay matrices that contain ferrous minerals may play an important role in long-term contaminant attenuation at many sites. While recent studies have identified and quantified these reactions in natural clays, verification of tools that can be used to estimate dechlorination rates in clays remain elusive. In addition, the extent to which processes identified at the bench-scale actually occur in the field remains largely unconfirmed. Data are thus needed to provide improved support for abiotic dechlorination as part of a viable natural attenuation remedy.

Approach/Activities. Bench-scale batch experiments using clay:water slurries were performed to evaluate the abiotic reductive dechlorination of trichloroethene (TCE) under anaerobic conditions, where generation of reduced gases were used to quantify first order rate constants. Natural clays used in this study were obtained from multiple chlorinated solvent impacted sites, and were characterized with respect to mineralogy used both X-ray diffraction (XRD) and multiple acid-based extractions. Batch experiments under aerobic conditions were performed to measure hydroxyl radical generation (facilitated by the presence of ferrous minerals), which in turn facilitate the oxidative dechlorination of TCE. Bench-scale testing was coupled with field data to verify that the abiotic processes observed in the laboratory were actually occurring in the field.

Results/Lessons Learned. Results to date showed that the observed first order dechlorination rate constants measured in the natural clays under anaerobic conditions were positively correlated to the ferrous mineral contents of the clay, as determined via dilute hydrochloric acid extraction. A notable exception to this correlation was observed for clays that contained pyrite. Experiments with clay containing pyrite showed substantial abiotic reductive dechlorination despite having a relatively low ferrous mineral content. The low ferrous mineral content was due to the fact that pyrite is not readily extracted via the dilute acid extraction employed in this study. However, when the ferrous mineral content associated with the pyrite was estimated using XRD, the correlation between first order dechlorination rate constant and ferrous mineral content aligned with those observed for the other clays. Initial field data also showed that reduced gases were present in clays with elevated abiotic dechlorination activity in the bench-scale experiments, thereby serving as another line evidence that these abiotic reductive dechlorination reactions are occurring in situ.

Measurable hydroxyl radical generation was observed in all the batch clay experiments under aerobic conditions. Field groundwater samples collected adjacent to the reactive clays showed that hydrogen peroxide (which is generated during the iron oxidation process) was present, indicating that these oxidative abiotic processes were occurring in situ at the clay-sand interface and thereby serving as a potential natural attenuation mechanism.

Overall, results of this study showed that readily applied bench-scale screening methods were useful for both identifying and quantifying naturally occurring abiotic dechlorination processes. Application of these tools has potential to reduce the time and effort needed to incorporate abiotic natural attenuation processes in site models.